SELF–DISCHARGE AND LOW TEMPERATURE CHARGE CHARACTERISTICS OF LI-ION CELLS

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ABSTRACT

Similar to other performance characteristics, self-discharge rates are impressive for Li ion cells compared to conventional rechargeable systems. However, the mechanisms underlying the self-discharge processes are not well understood. A significant portion of the self-discharge in a Li ion cell is believed to occur at the carbon anode, implying that it is a strong function of the nature of the electrolyte solution. In this paper, we present our single-electrode studies on the self-discharge characteristics of graphite electrodes in different electrolytes and at different temperatures. These measurements will be supported by the self-discharge characteristics of prototype Li ion sealed cells of various sizes.

Another aspect of particular relevance to the use of Li ion cells in NASA's future Mars missions is their performance at low temperatures. We have carried out various electrochemical studies to understand the rate-limiting processes in the charge and discharge reactions of Li ion cells. In particular, studies have focused on optimizing the charge conditions at low temperatures.

1.0 INTRODUCTION

The Li ion rechargeable cell, by virtue of its several desirable attributes, is emerging as the battery system of choice in several consumer applications, as well as, strategic defense and space applications. Several of NASA's future missions are either being enabled or enhanced by the use of Li ion batteries. Such applications would be further benefited by improvements in the low temperature performance and self-discharge characteristics in addition to the familiar aspects, i.e., specific energy and cycle life, that are being well addressed.[1-3]

Self-discharge processes in a Li ion cell are not easy to understand as in conventional (aqueous) systems. In the latter case, self-discharge is always induced by a parasitic reaction, e.g., oxygen evolution at the positive electrode or metallic corrosion at the negative electrode.[4] Alternately, certain electrolyte species sustain redox reactions at both the electrode and function as conjugate reaction to reactions involving active materials. Often, these processes are reversible making the capacity loss during self-discharge recoverable. In the case of a Li ion cell, there are no such parasitic processes either at the carbon anode or metal oxide cathode. Since the self-discharge rate appears to be more rapid at the carbon anode than the cathode, it is possible that the self-discharge of Li ion cell is initiated at the negative electrode and must be determined by the nature of electrolyte.[5] Accordingly, we have attempted to study the self-discharge reactions of carbon electrodes in half-cells with different electrolytes.

In addition, the self-discharge characteristics of sealed Li ion cells (1-20 Ah) have been determined to correlate with the electrolyte properties. Also, we attempted to verify the use of microcalorimetry to estimate the self-discharge.

Finally, in order to improve the low temperature performance of a Li ion cell, its charge characteristics at low temperatures have been examined. Specifically, the charge voltage has been increased at low temperatures, taking into account the negative temperature coefficient of the Li ion cell. These studies are aimed at constructing V_T (thermally compensated voltages)–like curves for Li ion cells, similar to Ni rechargeable systems.

2.0 EXPERIMENTAL

Half-cell studies were carried out in O-ring-sealed, glass cells containing jelly rolls of graphite (KS44) and $LiCoO_2$ electrodes with

polypropylene (Celgard 2500) separator and Li reference electrodes.

Sealed cells were fabricated in AA (400 mAh) and D (4 Ah) sizes at Wilson Greatbatch Ltd., Clarence, NY, using identical materials. Electrochemical measurements were made using EG&G Potentiostat/Galvanostat (and Solartron 1255 Frequency Response Analyzer for impedance measurements) interfaced with IBM PC, with Softcorr 352 (and M388 for impedance) software. All the electrolyte solutions employed were of battery grade.

3.0 RESULTS AND DISCUSSION

3.1 GRAPHITE HALF-CELLS

Six different electrolytes have been chosen for these studies, in the first phase, which include 0.75 M $LiPF_6$ in 1) equi-proportion ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC: DMC:DEC = 1:1:1), 2) EC-DMC (30:70), and 3) EC-DEC (30:70). The last three electrolytes contained 25 v% (to 75 v% of 1:1:1 solvent system) of quaternary solvent, i.e., methyl acetate (MA), ethyl acetate (EA) and dimethoxy ethane (DME), each of which showed yield electrolytes of appreciable conductivity at low temperatures.[1]

Interfacial characteristics of graphite anode in the above electrolytes, including the surface film (solid electrolyte interface – SEI) properties, stability, reversible and irreversible capacities and kinetics of lithium intercalation have been discussed in detail in our companion paper.[6] Briefly, the acetate additives formed highly resistive and protective surface films, accompanied by low irreversible capacities and poor kinetics. DME-based solutions, on the hand, showed the least protection, also evident from a high irreversible capacity. Among the other solvents, DMC-based solutions permitted stable surface film, with low irreversible capacity and poor kinetics, especially at low temperatures compared to EC-based solutions

After completing initial conditioning cycles and rate characterization tests, the carbon electrodes were fully charged and left under open circuit condition for four weeks. The self-discharge sustained during that period is illustrated in Fig.1, which shows the discharge curves before and after storage under identical conditions. As evident from the figure, the cells containing acetate additives (both MA and EA) showed poor capacity, after the rate

characterization studies. The interfacial resistance from the EIS measurements is significantly high, suggesting the formation a highly resistive surface film. Thus, initial results obtained in the present cell configuration and experimental conditions, indicate that these additives are not suitable in terms of interfacial stability and low temperature performance.

The degree of self-discharge in the cells is plotted as a function of the electrolyte composition in Fig.2. The self-discharge is generally in the range of 12-13% per month for carbonate based solvent systems (EC-DMC < EC-DMC-DEC < EC-DEC). With the DME additive, however, the self-discharge is considerably high, i.e., about 29% per month.

3.2 AC IMPEDANCE

In order to understand the changes occurring in the bulk and/or interfaces of the electrode during self-discharge, ac impedance measurements have been carried out on graphite electrodes in half-cells as well as in sealed D cells. Fig. 3 shows the EIS plots of graphite in different electrolytes before and after the self-discharge study. In all cases, there is an enlargement in the relaxation loop at high frequencies, which implies that there is a build up of interfacial layer during open circuit stand.[7] The EIS plots of sealed D cells also show similar trend in the initial stages of self-discharge (Fig. 4). In latter stages, however, there is an increase in the series resistance as well, which consists of the ohmic component from the electrodes/electrolyte. Upon recharging the cell the cell would not recover completely to its original interfacial conditions, which suggests that there is marginal irreversible decay in the interface, possibly due to deposits of electrolyte reaction product.

3.3. MICROCALORIMETRY

Microcalorimetry is often used to estimate the self-discharge and thus predict the shelf life of lithium primary cells.[8] The exothermic corrosion reaction is monitored in terms of heat output. In order to verify the applicability of this method to rechargeable Li ion cells, we attempted to correlate heat emission with self-discharge rates.

Fig. 5 shows the microcalorimetric (heat) out put of Li ion D cells as a function of storage time during self-discharge. As may be expected, the heat emission decreases exponentially with time, as also reported earlier.[9] Fitting it to a $y=X^n$ curve, the cumulated heat output over 60 days of

storage has been calculated. From a subsequent capacity determination, the cumulative heat loss of 67 mW corresponds to a capacity loss of 0.29 Ah. The self-discharge of the sealed cell is ~ 5%/month, lower than 12% observed in half-cell, possibly due to relatively higher amount of electrolyte in the latter.

Upon recharge the cell would show heat output significantly lower than that observed before the self-discharge measurements. This implies that in addition to the self-discharge process, another exothermic process contributes to the heat output. The latter may be a result of electrolyte degradation on the anode, as also evident in the EIS measurements. Microcalorimetry is thus not able to unambiguously measure rate of self-discharge; instead it can be used for a quantitative comparison of the reactivity of electrolytes with carbon anode, which we plan to study in future.

3.4 EFFECT OF CHARGE VOLTAGE

Since the cell voltage of a Li ion cell has a negative temperature coefficient, about -0.75 mV/°C, the charge voltage limit needs to be increased at least by the proportionate amount to ensure complete charging of cell at low temperatures. In addition, there could be kinetic implications for charge processes at low temperatures. In order to understand these, the effects of charge voltages on the charge capacity have been studied at different temperatures (Fig. 6). At ambient temperatures, capacity tends to level off at 3.6 V and increases subsequently. Similar plateau appears at higher charge voltages at low temperatures. The capacity at any charge voltage decreases with a decrease in the temperature. In other words, higher charge voltage needs to be applied to achieve complete charging at low temperatures. Based on these V_T curves will be generated for Li ion cells and will be corroborated by half-cell measurements.

4.0 CONCLUSIONS

Self-discharge of lithium ion cells is a mostly due to delithiation of carbon (rather than the conjugate process at the cathode) and involves a significant role by the electrolyte. Generally, solvents that enable the formation of stable surface films, cause less self discharge. There is an evidence of build up of surface film, part of which is irreversible, during self-discharge.

Owing to this, microcalorimetry is not too helpful in monitoring the self-discharge.

6.0 REFERENCES

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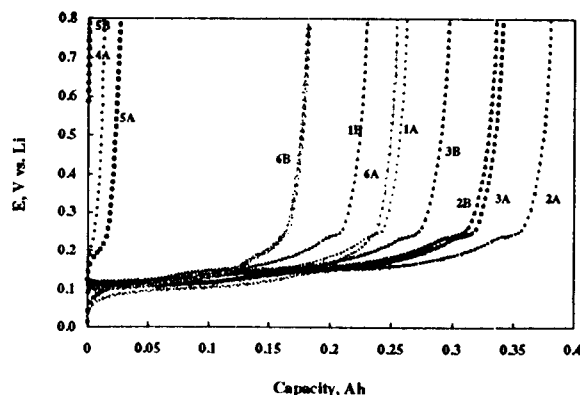9) J. A. Jeevarajan, A. Rokotondrainibe, A. J. Appleby and F. E. Little, Proc. IECEC (1997).

Fig. 1 : Discharge curves of graphite electrodes in 0.75 M LiPF$_6$ in 1) EC-DEC-DMC, 2) EC-DMC, 3) EC-DEC, 4) EC-DMC-DEC-MA, 5) EC-DMC-DEC-EA and 6) EC-DMC-DEC-DME , A) before and B) after 3 weeks of storage at 25°C.
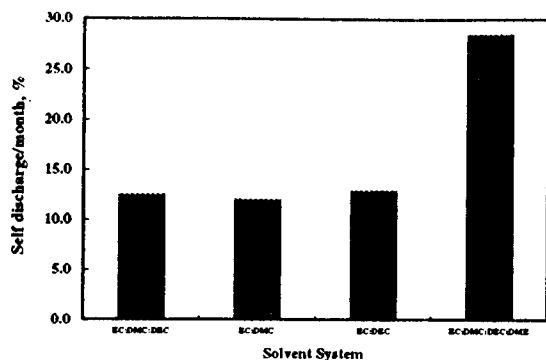
Fig. 2. Self-discharge of graphite electrodes in 0.75 M LiPF$_6$ in 1) EC-DEC-DMC, 2) EC-DMC, 3) EC-DEC, and 4) EC-DMC-DEC-DME at 25°C.

Fig. 5: Heat emissions (from microcalorimetry) for 1) cell 1 and 2) Cell 2 and 3) cumulative heat of Li ion D with 0.75 M LiPF$_6$ /EC-DEC-DMC electrolyte during self-discharge at 25°C.
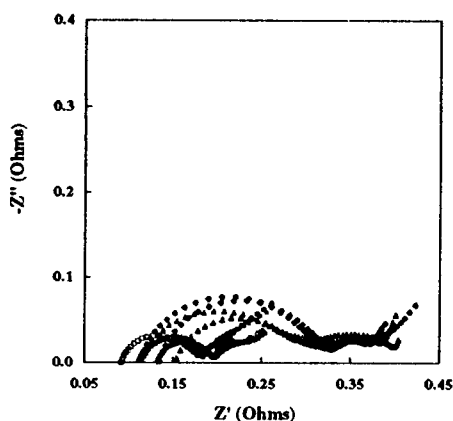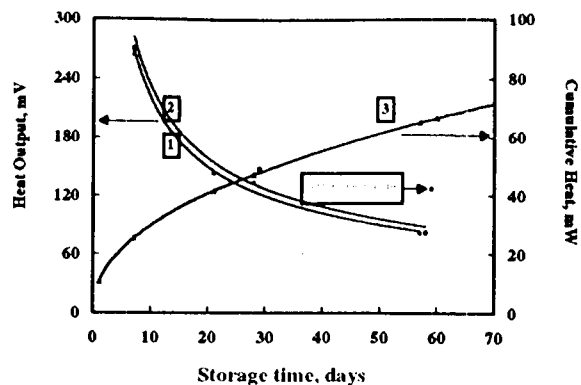

Fig.3 : AC impedance (Nyquist) plots of graphite in 0.75 M LiPF$_6$ in 1) EC-DEC-DMC (●), 2) EC-DMC (▲) 3) EC-DEC (◆) and 4) EC-DMC-DEC-DME (■), before (filled) and after (open) open-circuit stand.
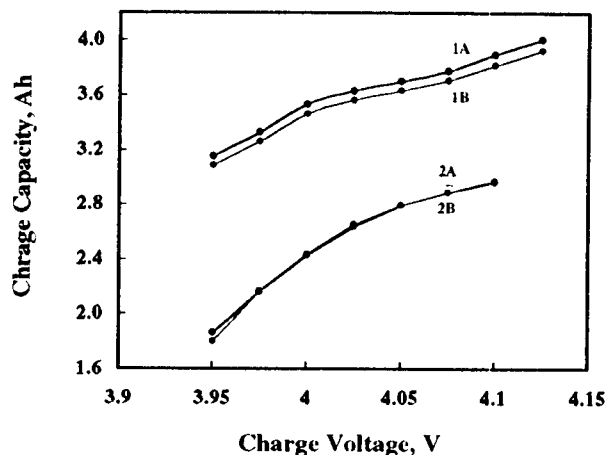

Fig. 6: Effect of charge voltage on the charge return A) and B) subsequent discharge capacity of a Li ion D cell 1) at 25 and 2) –20°C.

Fig. 4: Nyquist plots of Li ion D cell with 0.75 M LiPF$_6$/EC-DEC-DMC electrolyte after 1) 0, 2) 7, 3) 21, 4) 28 & 5) 57 days of self-discharge @ 25"C.